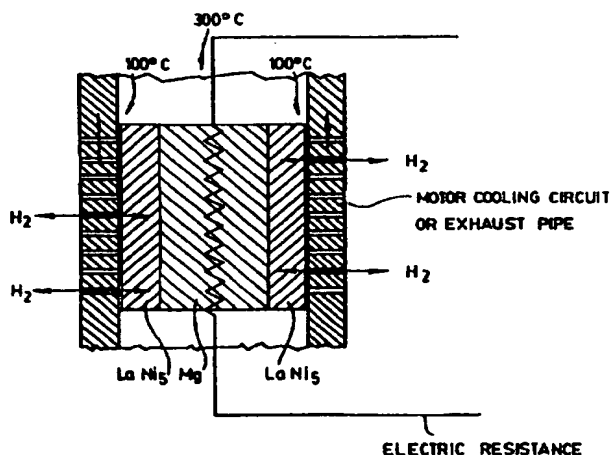




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/CA97/00035 (22) International Filing Date: 17 January 1997 (17.01.97)  (30) Priority Data: 08/587,588                      19 January 1996 (19.01.96)                      US  (71) Applicants: HYDRO-QUEBEC [CA/CA]; 75 West René-Lévesque Boulevard, Montreal, Quebec H2Z 1A4 (CA). MCGILL UNIVERSITY [CA/CA]; 845 West Sherbrooke Street, Montreal, Quebec H3A 2T5 (CA).  (72) Inventors: SCHULZ, Robert; 68 Bel Horizon, Ste-Julie, Quebec J0L 2S0 (CA). BOILY, Sabin; 9363 Iberville, Montreal, Quebec J0L 2S0 (CA). HUOT, Jacques; Apartment 404, 104 Boulevard Des Hauts-Bois, Ste-Julie, Quebec J0L 2S0 (CA). STROM-OLSEN, John; 443 Lansdowne Avenue, Westmount, Quebec H3Y 2V4 (CA). ZALUSKI, Leszek; 7242 Hamilton, Montreal, Quebec H4E 3E1 (CA). ZALUSKA, Alicja; 7242 Hamilton, Montreal, Quebec H4E 3E1 (CA).  (74) Agent: ORLHAC, Thierry; Robic, 55 St-Jacques, Montreal, Quebec H2Y 3X2 (CA).	(81) Designated States: CA, CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report. With amended claims and statement.	

(54) Title: NANOCRYSTALLINE COMPOSITE FOR HYDROGEN STORAGE



## (57) Abstract

Disclosed is a nanocrystalline composite useful for hydrogen storage, which provides optimum hydrogenation conditions along with high hydrogen storage capacity. This composite is the combination of at least one high temperature metal hydride as Mg or Mg<sub>2</sub>Ni, which has a high hydrogen storage capacity by weight but requires high temperatures for hydrogen absorption and desorption, with at least one low temperature metal hydride such as FeTi, LaNi<sub>5</sub>, Nb, Mn or Pd, which has a low hydrogen storage capacity by weight but does not require high temperatures for hydrogen absorption and desorption. The high and low temperature metal hydrides are in direct contact with each other and each in the form of a nanocrystalline powder or layer. This composite is particularly useful as a hydrogen supply source for hydrogen-fueled vehicles.

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**NANOCRYSTALLINE COMPOSITE FOR HYDROGEN STORAGE****BACKGROUND OF THE INVENTION****5                   a)     Field of the invention**

The present invention relates to a nanocrystalline composite for use to store hydrogen.

The invention also relates to methods of preparing such composite and to their use.

10

**b)     Brief description of the prior art**

The main reasons to develop and use a composite are essentially (1) to take advantage of the unique properties of each component of the composite and (2) to profit from its complex (multi-component) microstructure.

15                   In the case of a composite for use to store hydrogen, the purpose of combining two or more hydrogen carriers is essentially to be able to modify the hydrogenation/dehydrogenation properties of the resulting composite in such a way as to provide a wider range of operational conditions.

Although a large variety of hydrogen carriers exists, which mainly  
20   consist of metal hydrides operating at temperatures ranging between -40°C and 500°C, there is no suitable hydrogen carrier which provides optimum hydrogenation conditions along with a high hydrogen storage capacity. By way of examples, in the case of a hydrogen-fueled vehicle, such "optimum" hydrogenation conditions would be an ability to absorb/desorb hydrogen at a  
25   temperature of about 150°C, while a "high" hydrogen storage capacity would be an ability for the carrier to store more than 3% by weight of hydrogen.

So far, there is no hydrogen carrier which can meet both of these requirements. Indeed, all the hydrogen carriers which can operate at temperatures lower than 100°C have a hydrogen storage capacity by weight  
30   that is too low to be effective in transportation. For example, FeTi has a storage capacity of 1.9 wt % while LaNi<sub>5</sub> has a capacity of 1.3 wt%. On the other hand, all the hydrogen carriers which exhibit a high hydrogen storage capacity, such as, for example Mg<sub>2</sub>Ni which has a capacity of 3.6 wt% or Mg

which has a capacity of 7.65 wt%, require temperatures higher than 300°C for hydrogenation/dehydrogenation cycling. Of course, the need for high temperature (usually ranging from 300 to 400°C) for absorption/desorption decreases the efficiency of such carriers and the potential development and use of vehicles using hydrogen as a fuel.

In copending U.S. patent application serial Nos. 08/382,776 and 387,457 filed on February 2 and 13, 1995, respectively in the name of the same assignees, a new generation of hydrogen carriers is disclosed, which consist of nanocrystalline metal hydride powders incorporating or not a catalyst.

More particularly, U.S. application serial No. 08/387,457 discloses a powder of an alloy of Ni and Mg, La, Be or Ti, consisting of crystallites having a grain size lower than 100 nm and preferably lower than 30 nm and a crystalline structure allowing hydrogen absorption. This powder is preferably obtained by mechanical grinding and may consist of crystallites of  $Mg_2Ni$ ,  $LaNi_5$  or of Ni-based alloys of Be or Li. It is particularly useful for storing and transporting hydrogen, since it requires no or only one single activation treatment at low temperature to absorb hydrogen and its kinetic of absorption and diffusion of hydrogen is fast.

U.S. application serial No. 08/382,776 discloses a very light-weight, Mg and Be-based material which has the ability to reversibly store hydrogen with very good kinetics. This material is of the formula:



wherein:

M is Mg, Be or a combination of them;

A is an element selected from the group consisting of Li, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Y, Zr, Nb, Mo, In, Sn, O, Si, B, C and F

D is a metal selected from the group consisting of Fe, Co, Ni, Ru, Rh, Pd, Ir and Pt (preferably Pd);

x is a number ranging from 0 to 0.3; and

y is a number ranging from 0 to 0.15.

This material is in the form of a powder of particles of the formula  $M_{1-x}A_x$  as defined hereinabove, each particle consisting of

nanocrystalline grains having an average size of 3 to 100 nm or having a nanolayered structure with a layer spacing of 3 to 100 nm. Some of these particles have clusters of metal D attached thereto, with an average size ranging from 2 to 200 nm.

5                   The nanocrystalline powders disclosed in both of the above U.S. applications overcome most of the drawbacks of the conventional hydrides, including:

- the problems of poisoning by oxidation;
- the need for activation; and
- 10       -       too slow kinetics of hydrogenation/dehydrogenation.

The latter point is essential since outstanding kinetics of hydrogen uptake permits to decrease significantly the effective operational temperature of, for example, the Mg-based hydrides, to a range inaccessible for conventional, polycrystalline materials (for example 200 to 250°C).

15                   In spite of the above advantages, many potential applications for hydrogen carriers, especially, metal hydrides, require a cold start-up of the hydrogen-fueled devices, which means ambient temperature for the initiation of the process, with the possibility of gradually switching to higher temperatures as the device warms up.

20

#### **SUMMARY OF THE INVENTION**

The object of the present invention is to provide a new product hereinafter called "nanocrystalline composite", which has all the advantages  
25 of the above mentioned nanocrystalline hydrides, but also allows "designing" of the hydrogenation/dehydrogenation performance to meet a given specification.

This object is achieved with a nanocrystalline composite particularly useful for hydrogen storage, which comprises in combination:

- 30                   a)       at least one first hydrogen carrier hereinafter called "high temperature metal hydride", which has a high hydrogen storage capacity but requires high temperatures for hydrogen absorption and desorption; and

b) at least one second hydrogen carrier hereinafter called "low temperature metal hydride", which has a low hydrogen storage capacity but does not require high temperatures for hydrogen absorption and desorption.

5 In accordance with the invention, the high and low temperature metal hydrides are in direct contact with each other and each in the form of a nanocrystalline powder.

This powder consists of particles and the term "nanocrystalline" as used herein means that the particles have nanocrystalline grains with an  
10 average size of 3 to 100 nm, or a nanolayered structure with a layer spacing of 3 to 100 nm.

By way of non-restrictive examples, the high temperature metal hydrides may consist of Mg,  $Mg_2Ni$  and possibly Be, and Li alloys while the low temperature metal hydride may consist of alloys such as FeTi and  $LaNi_5$ , or  
15 metals such as Nb, V, Na, Cs, Mn and Pd.

As can be understood, the main idea of the invention is to utilize at least two different kinds of metal hydrides which operate at different temperatures, thereby allowing for multistage hydrogenation/dehydrogenation cycles.

20 The low-temperature metal hydride (for example FeTi or  $LaNi_5$ ) is responsible for the cold start-up of the device when use is made of the composite according to the invention as a source of fuel. This low-temperature metal hydride which may represent 30% only of the total weight of the composite, does not significantly reduce the total hydrogen storage  
25 capacity of the system. It releases hydrogen at ambient temperature, if only hydrogen pressure in the container is lower than a certain value (for example less than 5 bars). The initially desorbed hydrogen may be used immediately for combustion purposes.

After the device is started up, especially when such device is a  
30 combustion engine, like the motor of a car, temperatures high enough will be provided by the same to carry on desorption from the high-temperature metal hydride ( $Mg$ ,  $Mg_2Ni$  or their alloys with other elements), which is the other component of the composite.

During cooling down of the device after it has been switched off, the combination of two different metal hydrides also has an additional advantage. Desorption from the high-temperature hydride may still proceed after switching-off of the device, if the temperature is not immediately  
5 reduced. In such a case, any excess of unused hydrogen gas will be absorbed by the low-temperature hydride in contact with the high temperature metal hydride in the course of cooling, thereby allowing for the next cold start-up of the device.

In the above description, reference has been made to the supply  
10 of a hydrogen-operated car motor as a potential use of the invention. Of course, it should be understood that such an application is not the only one, as the same advantages of the composite according to the invention could also benefit to heat pumps, generators and the like.

The invention, its methods of preparation and its use and  
15 advantages will be better understood upon reading the following non-restrictive detailed description thereof.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

In the accompanying drawings:

20 Figure 1 is a schematic, cross-sectional representation of a nanocrystalline alloy according to the invention, in the form of compressed layers of high and low temperature nanocrystalline metal hydrides;

Figure 2 is a schematic, cross-sectional representation of a nanocrystalline alloy according to the invention, in the form of a core made of  
25 a high temperature metal hydride coated with a surface layer of a low temperature metal hydride; and

Figure 3 is a diagram giving the percentage by weight of hydrogen absorbed in a nanocrystalline composite of Mg and FeTi as a function of time at a temperature ranging from the room temperature to 200°C under  
30 a pressure of 9 bars.

#### **DETAILED DESCRIPTION OF THE INVENTION**

As aforesaid, the nanocrystalline composite according to the invention is particularly useful for hydrogen storage, inasmuch as it provides optimum hydrogenation conditions along with a high hydrogen storage capacity.

5 This composite is made of two or more components including:

a) at least one first hydrogen carrier hereinafter called "high temperature metal hydride", which has a high hydrogen storage capacity by weight but requires high temperatures for hydrogen absorption and desorption; and

10 b) at least one second hydrogen carrier hereinafter called "low temperature metal hydride", which has a low hydrogen storage capacity by weight but does not require high temperatures for hydrogen absorption and desorption.

As high temperature metal hydride, use can be made of Mg or  
15  $Mg_2M$ . Both of these materials are able to absorb a high amount of hydrogen (3.6 wt% in the case of  $Mg_2Ni$ ; 7.65 wt% in the case of Mg), but at high temperatures only (higher than 200°C).

As low temperature metal hydride, use can be made of alloys such as FeTi or  $LaNi_5$ , or metals such Nb, V, Na, Cs, Mn and Pd. All of these  
20 materials are able to absorb and desorb hydrogen at low temperatures ranging from ambient temperature to 100°C, but in much smaller amount in weight % than Mg or  $Mg_2Ni$ . Thus, for example, FeTi may absorb up to 1.9 wt % of hydrogen whereas  $LaNi_5$  may absorb up to 1.3 wt% of hydrogen only.

In accordance with a very important aspect of the invention, the  
25 high and low temperature metal hydrides must be in direct contact with each other and each of them must be in the form of a nanocrystalline powder or lawyer. This nanocrystalline structure is essential in obtaining the expected performance in hydrogenation/dehydrogenation cycles. Indeed, very good kinetics are achieved by enhanced hydrogen diffusion on grain boundaries and  
30 defects.

Each of these powders can be prepared directly from chunks of metal(s). This direct preparation can be carried out as is disclosed in the above referenced U.S. patent application serial Nos. 08/382,776 and 387,457, both



of which are incorporated herewith by reference.

More particularly, such direct preparation can be carried out in a very simple yet efficient manner, by merely grinding at ambient temperature under an inert atmosphere, a powder of the metal to be reduced to a nanocrystalline form, or a mixture of powders of two different metals, such as Ni and Mg, in amounts selected to obtain the requested composition. To be efficient, this grinding must be carried out under high energy conditions for several hours, typically 20 h for reducing the particle size of the metal to the requested value, and from 30 to 40 h for forming an alloy of metal and reducing its particle size to the requested value. This grinding allows the preparation by mechanical alloying of the requested alloy from powders of Ni and of the other metal and at the same time reduces the crystal size to the requested value.

From a practical standpoint, this intense grinding can be carried out with a high energy ball milling machine. By way of examples of such ball milling machines, reference can be made to those sold under the trademarks SPE 8000, FRITCH and ZOZ.

In the case where powders of different metals are used, such an intense grinding under an inert atmosphere (like argon) causes the different metals to react while the powders are ground, and leads to the formation of the corresponding crystalline alloy particles. Such is particularly interesting since this allows for the direct synthesis of alloys in the solid state, such as for example,  $Mg_2Ni$ , that are usually very difficult to obtain by melting and cooling.

In order to further improve the quality and efficiency of the nanocrystalline powders used in accordance with the invention, a small amount typically of 1% by weight, of a material capable of catalysing the dissociation of the hydrogen molecule, such as, for example, palladium, can and should preferably be applied onto the surface of the nanocrystalline particles. This material can be applied in a very simple manner, by grinding for a shorter period of time the synthesized nanocrystalline particles with a powder of the catalyst material. This subsequent grinding causes clusters of the catalyst, like palladium, to be deposited onto the surface of the crystalline particles. It is however compulsory that this supplemental grinding be not too long, since,

otherwise, a new intermetallic alloy could be formed.

After every one of the powders of high and low temperature metal hydrides have been prepared, they must be combined together to form the requested nanocrystalline composite.

- 5 In accordance with a first embodiment of the invention, the composite can be prepared by intermixing the powders of low and high temperature metal hydrides and by compressing the resulting mixture at ambient or low temperature. This compression step is important for two reasons. First of all, it ensures that both metal hydrides are in direct contact.
- 10 Such is important because the low-temperature hydride has a catalytic effect on the absorption of the high-temperature hydride. Besides, the particles of the low-temperature hydride prevent sintering of the high-temperature hydride at elevated temperatures. The high-temperature hydrides are usually Mg-based and are sensitive to sintering at elevated temperatures. This is a disadvantage
- 15 because sintering reduces the active surfaces and interfaces available for hydrogen absorption/desorption. Such disadvantage is partly overcome thanks to the presence of the low-temperature hydride in the composite.

- The intermixing (or admixture) of the two powders can be made in the same grinder as was used for their preparation and can be combined to
- 20 a supplemental grinding step to further reduce the size of the particles.

- In this connection, it is worth mentioning that this method of preparation is substantially different from the one disclosed by Liang Guoxian et al in their article entitled "Hydrogen absorption and desorption characteristics of mechanically milled Mg-35 wt% FeTi<sub>1.2</sub> powders" (Journal
- 25 of Alloys and Compounds, not published yet). Indeed, in the method disclosed in this article, the FeTi alloy is first prepared by arc melting and crushed into a powder of less than 80 mesh. Then, this powder is mixed with a Mg powder and the resulting mixture is subjected to "intensive" mechanical grinding in an attritor ball-mill under an inert atmosphere. The resulting product is in the form
- 30 of nanocrystalline particles but is not a mixture of separate particles of the original Mg and FeTi powders, as is obtained and actually required in the present invention. Rather, in the method of Liang Guoxian et al, the resulting particles essentially consist of an alloy of Mg, Fe and Ti, as, during the grinding

step carried out on the powders originally in a non-nanocrystalline form, interdiffusion occurs between these powders (this mechanism is actually the same as the one used to produce the nanocrystalline alloy powders disclosed in the above mentioned U.S. patent applications).

5 Even in the case where, in accordance with the present invention, the mixture of nanocrystalline powders of high and low temperature metal hydrides is subjected to a supplemental grinding step, such will be different from what is disclosed by Liang Guoxian et al. Indeed, when the powders used as starting materials are already in a nanocrystalline form, further grinding will  
10 not cause interdiffusion of the alloys and/or metal, as occurs when one starts from conventional crystalline particles. As a matter of fact, in the invention, only a fine dispersion of nanocrystalline particles will be obtained, with no or very little modification of the physical characteristics of each material.

If this first embodiment has proved to be efficient (see the  
15 following example), it has also been found that, with this kind of composite made of intermixed powders, hydrogen may be "trapped" in the high temperature metal hydride during desorption at low temperature. To prevent such drawback, and ensure that a sufficient amount of hydrogen be always present in the low temperature metal hydride, it would be advisable that the  
20 low temperature metal hydride (VIZ.  $\text{LaNi}_5$ ,  $\text{FeTi}$ , ...) surrounds and encloses the high temperature metal hydride (VIZ.  $\text{Mg}$ ,  $\text{Mg}_2\text{Ni}$ ).

Thus, in accordance with a second embodiment of the invention, the composite can be prepared in such a manner as to form a sandwich structure comprising an inner layer made of a compressed nanocrystalline  
25 powder of a high temperature metal hydride, such as for example  $\text{Mg}$ , which is compressed between two opposite outer layers, each of which is made of a compressed nanocrystalline powder of a low temperature metal hydride, such as for example  $\text{LaNi}_5$ . This embodiment is shown in Fig. 1 of the accompanying drawings.

30 The sandwich structure shown in Fig. 1 can be obtained by pouring a given amount of nanocrystalline  $\text{LaNi}_5$  powder into the matrix of a mold and subjecting the so-poured amount to a light pressure to form a first layer. Then, the mold is opened and an amount of a nanocrystalline  $\text{Mg}$  powder

is poured onto the first layer and pressed to form a second layer onto the first one. Advantageously, an electric resistance can be inserted into the mold together with the Mg powder so as to be embedded into the same as shown in Fig. 1. Finally, the mold is opened again and another amount of  
5 nanocrystalline  $\text{LaNi}_5$  powder is poured into the mold onto the second compressed layer and pressed to form a third layer on top of the second one.

The resulting composite is in the form of a sandwich "panel" containing a core made, of the high temperature metal hydride, which is squeezed between two outer layers of the low temperature metal hydride.

10 In use, lowering of the external pressure surrounding this composition will allow immediate desorption and release of the hydrogen contained in the outer layers of  $\text{LaNi}_5$ . This will allow for starting up the engine. As soon as the same starts heating up, its heat and electrical energy produced by an alternator connected to the same will become available to heat the core  
15 of Mg and thus allow for the hydrogen contained in greater amount into this core, to be desorbed.

In accordance with a third embodiment of the invention, another kind of effective, non-homogeneous nanocrystalline composite can be prepared in such a manner that each particle is in the form of a core made of a high  
20 temperature metal hydride such as for example  $\text{Mg}_2\text{Ni}$  that is coated by a surface layer of a low temperature metal hydride such as, for example,  $\text{LaNi}_5$ . This third embodiment is illustrated in Fig. 2 of the accompanying drawings.

Such a structure can be obtained in different ways.

A first one basically consists in preparing a nanocrystalline  $\text{Mg}_2\text{Ni}$   
25 alloy by high energy mechanical grinding, as is disclosed in U.S. patent application serial No. 08/387,457. Advantageously, a catalyst should be added to the starting metal powders to form catalyst clusters onto the surface of the resulting alloy, as is also disclosed in the above application. During this grinding step, additional Ni will also be added to the mixture in order to over-  
30 saturate the alloy with Ni. Then, pure La will be added to the alloy and the resulting mixture is subjected to further high energy mechanical grinding. Since La in a metal state is more ductile than the nanocrystalline alloy, it will coat the alloy. After such is done, the coated particles will be subjected to a thermal

treatment (annealing). Such will cause the Ni surplus in the alloy to diffuse toward the external La coating and then form particles having a  $Mg_2Ni$  core and a  $LaNi_5$  external coating.

Another way of obtaining this structure would be to subject to  
5 a high energy mechanical grinding, a mixture of Mg particles with particles of another metal known to absorb hydrogen at low temperature, like Nb, V, Na, Cs, Mn or Pd. These other metals are known to be "naturally" non-miscible with Mg. However, with such a high energy grinding, an over-saturated solution of both Mg and the other metal will be formed. Subsequent heat  
10 treatment (annealing) of the solution will cause the other metal, for example Nb, to diffuse toward the external surface of the particles, thereby resulting in particles having a central core mainly of Mg and an external coating mainly of Nb. Temperature during the annealing should be kept low enough so that excessive grain growth do not occur during heat treatment, the microstructure  
15 remaining nanocrystalline.

As aforesaid, the nanocrystalline composite according to the invention can be used to operate a hydrogen-fueled vehicle. By way of example, a composite combining from 15 to 30 wt %, preferably 20 wt % of a low temperature hydrogen carrier with from 95 to 70%, preferably 80 wt %,   
20 of a high temperature hydrogen carrier will allow starting up of a cold motor thanks to the low temperature metal hydride, and subsequent operation of the motor over a long distance thanks to the high storage capacity of the high temperature metal hydride that will start become operative and useful as soon as the motor is hot. So, for a same amount of hydrogen-absorbing medium, a  
25 much better efficiency will be achieved.

#### Example

A nanocrystalline Mg-Fe Ti composite was prepared by mixing nanocrystalline powders of Mg and FeTi (70 wt % and 30 wt % respectively)   
30 prepared in a high energy ball-milling machine FRITCH. During the mixing step that was carried out in the same machine, 0.8 wt % of palladium was added as a catalyst.

Then, the resulting mixture was compressed into a tablet which was placed in the reaction chamber of an automated gas titration apparatus. The reaction chamber was evacuated and hydrogen gas was admitted under a pressure of 9 bars at room temperature. Temperature cycling was carried on  
5 between room temperature and a temperature of 200°C to achieve absorption/desorption of the Mg-based alloy.

Figure 3 shows the result of this two-stage hydrogenation process. FeTi absorbed hydrogen at room temperature and the Mg-based alloy at high temperature. The total hydrogen storage capacity of the composite  
10 was above 4 wt %.

**WHAT IS CLAIMED IS:**

1. A nanocrystalline composite for hydrogen storage, said composite comprising in combination:
  - 5 a) at least one first hydrogen carrier hereinafter called "high temperature metal hydride", which has a high hydrogen storage capacity by weight but requires high temperatures for hydrogen absorption and desorption; and
  - b) at least one second hydrogen carrier hereinafter called  
10 "low temperature metal hydride", which has a low hydrogen storage capacity by weight but does not require high temperatures for hydrogen absorption and desorption, said at least one high temperature metal hydride and said at least one low temperature metal hydride being in contact with each other and each in the form of a nanocrystalline powder.  
15
2. The nanocrystalline composite of claim 1, wherein the nanocrystalline powder of said at least one high temperature metal hydride is in admixture with the nanocrystalline powder of said at least one low temperature metal hydride, and said admixed powders are compressed.  
20
3. The nanocrystalline composite of claim 1, wherein the nanocrystalline powder of said at least one high temperature metal hydride is compressed and forms an inner layer that is compressed between two outer layers of the nanocrystalline powder of said at least one low temperature metal  
25 hydride, which is also compressed.
4. The nanocrystalline composite of claim 3, wherein the inner layer made of said nanocrystalline powder of said at least one high temperature metal hydride incorporates a heating element.  
30
5. The nanocrystalline composite of claim 1, wherein the nanocrystalline powder of said at least one high temperature metal hydride is in the form of cores coated by a surface layer of the nanocrystalline powder

of said at least low temperature metal hydride.

6. The nanocrystalline composite of any one of claims 1 to 5, wherein said at least one high temperature metal hydride is selected from the group consisting of Mg, Mg<sub>2</sub>Ni and Be and Li alloys and said at least one low temperature metal hydride is selected from the group consisting of FeTi, LaNi<sub>5</sub>, Nb, V, Na, Cs, Mn and Pd.

7. The nanocrystalline composite of claim 6, comprising from 70 to 95% by weight of said at least one high temperature metal hydride and from 15 to 30% by weight of said at least one low temperature metal hydride.

8. The nanocrystalline composite of claim 6, wherein the nanocrystalline powders of said at least one high temperature metal hydride and said at least one low temperature metal hydride, include a hydrogen dissociation catalyst.

9. The nanocrystalline composite of claim 8, wherein said catalyst consists of clusters of Pd.



**AMENDED CLAIMS**

[received by the International Bureau on 17 June 1997 (17.06.97);  
original claims 1-9 replaced by amended claims 1-7 (2 pages)]

1. A nanocrystalline composite for hydrogen storage, said composite  
5 comprising in combination:
- a) from 70 to 95% by weight of at least one first hydrogen carrier  
hereinafter called "high temperature metal hydride", which has a high hydrogen  
storage capacity by weight but requires high temperatures for hydrogen absorption  
and desorption, said at least one high temperature metal hydride being selected  
10 from the group consisting of Mg, Mg<sub>2</sub>Ni and Be and Li alloys; and
- b) from 5 to 30% by weight of at least one second hydrogen  
carrier hereinafter called "low temperature metal hydride", which has a low  
hydrogen storage capacity by weight but does not require high temperatures for  
hydrogen absorption and desorption, said at least one low temperature metal  
15 hydride being selected from the group consisting of FeTi, LaNi<sub>5</sub>, Nb, V, Na, Cs, Mn  
and Pd;
- characterized in that:
- said at least one high temperature metal hydride and said at least one  
low temperature metal hydride are in contact with each other; and  
20 said at least one high temperature metal hydride and said at least one  
low temperature metal hydride are each in the form of a nanocrystalline powder.
2. The nanocrystalline composite of claim 1, characterized in that  
the nanocrystalline powder of said at least one high temperature metal hydride is  
25 in admixture with the nanocrystalline powder of said at least one low temperature  
metal hydride, and said admixed powders are compressed.
3. The nanocrystalline composite of claim 1, characterized in that  
the nanocrystalline powder of said at least one high temperature metal hydride is  
30 compressed and forms an inner layer that is compressed between two outer layers  
of the nanocrystalline powder of said at least one low temperature metal hydride,  
which is also compressed.

4. The nanocrystalline composite of claim 3, characterized in that the inner layer made of said nanocrystalline powder of said at least one high temperature metal hydride further comprises a heating element.
5. The nanocrystalline composite of claim 1, characterized in that the nanocrystalline powder of said at least one high temperature metal hydride is in the form of cores coated by a surface layer of the nanocrystalline powder of said at least low temperature metal hydride.
6. The nanocrystalline composite of any one of claims 1 to 5, characterized in that the nanocrystalline powders of said at least one high temperature metal hydride and said at least one low temperature metal hydride include a hydrogen dissociation catalyst.
7. The nanocrystalline composite of claim 6, characterized in that said catalyst consists of clusters of Pd.

**STATEMENT UNDER ARTICLE 19 PCT**

In order to better emphasize the original features of the present invention, the subject matter of former claims 6 and 7 has been incorporated into former claim 1. Moreover, former claim 1 has been cast into two parts, including a preamble and a characterizing part in which the original features of the invention are emphasized.

As a result:

- new claim 1 is a combination of former claims 1, 6 and 7;
- new claims 2 to 5 substantially correspond to former claims 2 to 5; and
- new claims 6 and 7 substantially correspond to former claims 8 and 9.

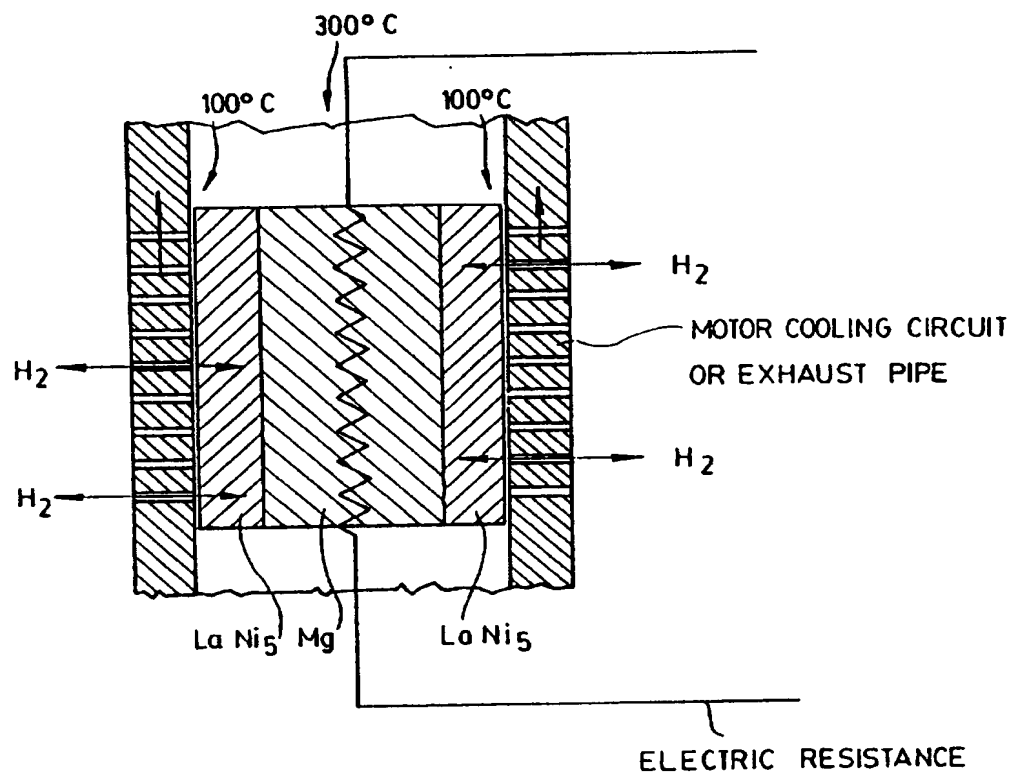
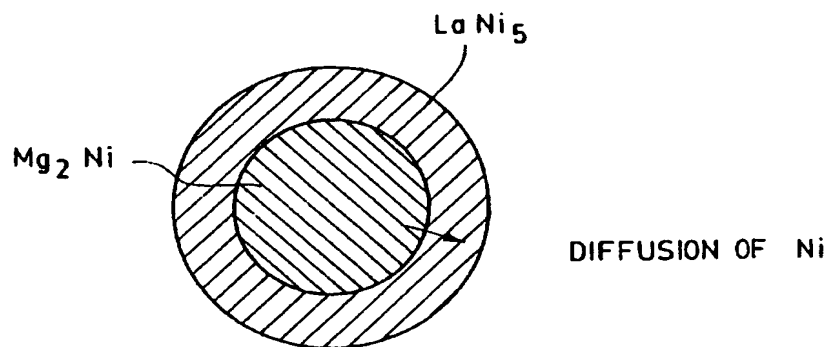
As will be noticed, the term "wherein" used in all the sub-claims has been replaced by the expression --characterized in that--.

The term "incorporates" used in claim 4 has also been replaced by the expression --further comprises--.

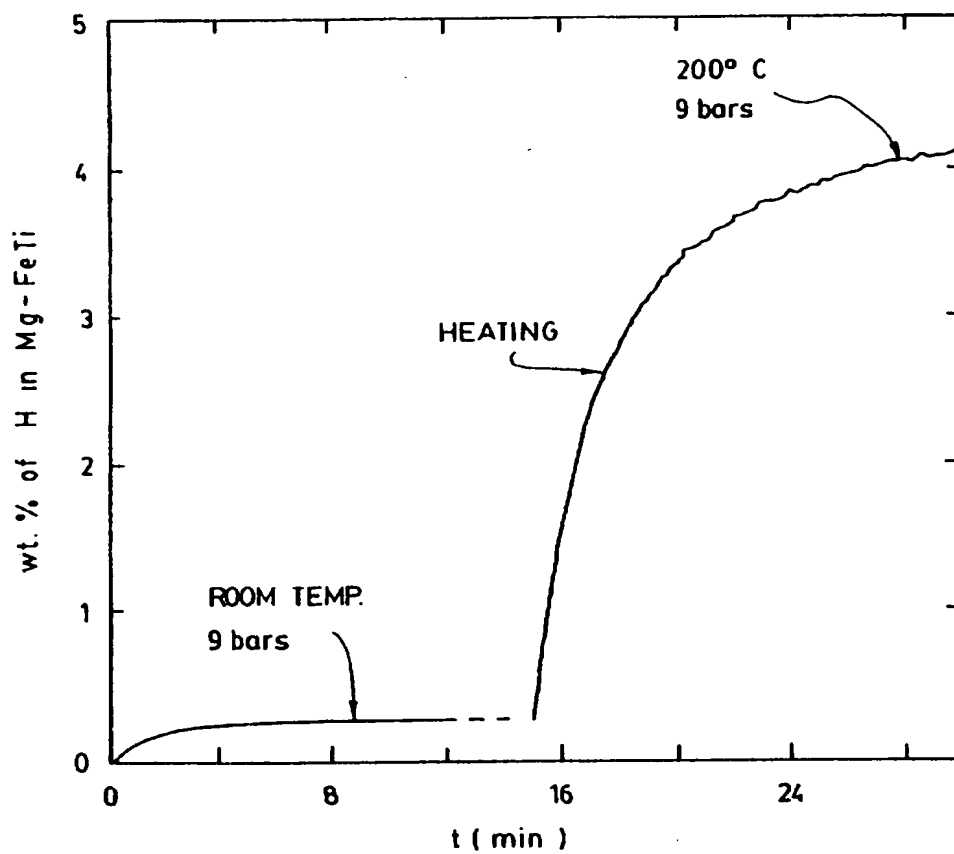
Moreover, the dependency of former claim 8, now renumbered claim 6, has been broadened.

It is worth mentioning that obvious clerical errors should be corrected on page 2, line 6 (08/382,776) and on page 4, line 14 and page 10, line 5 (LaNi<sub>5</sub>).

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FIG. 1FIG. 2

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FIG. 3

# INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/CA 97/00035

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C01B3/00 H01M8/06 C22C45/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOURNAL OF ALLOYS AND COMPOUNDS, vol. 223, no. 1, 15 May 1995, pages 111-114, XP000509211 GUOXIAN L ET AL: "HYDROGEN ABSORPTION AND DESORPTION CHARACTERISTICS OF MECHANICALLY MILLED MG-35WT.%FETI1.2 POWDERS" cited in the application see the whole document ---	1,6-9
Y	EP 0 671 357 A (HYDRO QUEBEC ;UNIV MCGILL (CA)) 13 September 1995 see the whole document ---	1,3,5-9
Y	DE 44 05 497 A (MAZDA MOTOR) 25 August 1994 see column 1, line 14 - column 2, line 59 see column 3, line 25 - column 4, line 32 see examples ---	1,3,5-9
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

14 April 1997

Date of mailing of the international search report

21.04.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 559 (C-0787), 12 December 1990 & JP 02 240225 A (SANYO ELECTRIC CO LTD), 25 September 1990, see abstract	1
A	--- JOURNAL OF ALLOYS AND COMPOUNDS, vol. 210, 1 August 1994, pages 37-43, XP000458108 ORIMO S ET AL: "SYNTHESIS OF FINE COMPOSITE PARTICLES FOR HYDROGEN STORAGE, STARTING FROM MG.YN12 MIXTURE" see the whole document -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 97/00035

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0671357 A	13-09-95	CA 2117158 A	08-09-95
		JP 7268403 A	17-10-95
DE 4405497 A	25-08-94	JP 6299272 A	25-10-94
		US 5536586 A	16-07-96



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